

Development of low-background vacuum extraction and graphitization systems for ^{14}C dating of old (40–60 ka) samples

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Abstract

At the University of Arizona's Desert Laboratory, we recently constructed new low-background vacuum extraction and graphitization systems that are dedicated to preparing old (40–60 ka) samples for ^{14}C dating. These systems are designed to minimize the amount of contaminant carbon, specifically atmospheric carbon, that is introduced to a sample during laboratory processing. Excluding contaminants is particularly important for ^{14}C dating of old samples because the impact of contamination increases with sample age. In this study, we processed 20 pretreated and 4 untreated aliquots of Ceylon graphite (a naturally-occurring geological graphite) to determine the total procedural background level, and hence the practical limit, of our systems. Samples were heated under vacuum at 240 °C for 1 h to drive off water vapor and other atmospheric gases, and then combusted in ultra-high-purity (UHP) O_2 at 500 and 850 °C to monitor the removal of contaminants and to ensure complete combustion. After SO_x , NO_x , and halide species were removed, sample CO_2 was converted to graphite via catalytic reduction of CO. Fe and Zn powders used in the graphitization process were oxidized, “scrubbed”, and reduced with UHP O_2 , He, and H_2 , respectively, to remove sorbed atmospheric C species. Graphite targets were stored in UHP Ar until measurement by accelerator mass spectrometry (AMS) to avoid potential interaction with atmospheric gases. Based on the AMS results, the background level of our system is characterized by a nonlinear inverse relationship with sample mass (adjusted $R^2 = 0.75$; $n = 24$). For a 1 mg graphite target, the total procedural blank, including chemical pretreatment, combustion, cleanup, graphitization, storage, and AMS measurement, is 0.05 ± 0.01 pMC (2σ), equivalent to a ^{14}C “age” of 61.1 ± 1.8 ka. This should not be taken as the upper limit of our system, however, because if the ^{14}C activity of a sample is statistically indistinguishable from the appropriate mass-dependent blank value at the 95% confidence level (2σ), then its age is considered to be “infinite”. Thus, for a 1 mg target, the practical limit of our system is actually ~ 55 ka; for a 0.5 mg target, the practical limit is ~ 50 ka. Although our extraction system can accommodate inorganic samples (e.g., calcite, aragonite), the above limits are only applicable to geological graphite, charcoal, and organic samples that are processed via combustion. Future work will be directed toward determining the appropriate background levels for inorganic materials.

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1. Introduction

Radiocarbon laboratories worldwide routinely provide reliable ^{14}C dates in the 0–40 ka (thousands of ^{14}C years before present) range to the geological and archeological communities. However, geochronologists widely recognize that the reliability of ^{14}C dating quickly degrades toward

the end of this range and that ^{14}C ages older than ~ 40 ka are often inaccurate. In practice, analytical measurement limits for ^{14}C dating by accelerator mass spectrometry (AMS) are typically on the order of 60 ka, but reliable AMS dates approaching this limit have yet to be realized. The reason is simple, but potential solutions are complex: the amount of “original” ^{14}C used for age estimation in old samples (> 40 ka) is very small ($< 1\%$ of the initial total) and is extremely sensitive to contamination that may be introduced during burial, sampling, and/or laboratory processing.

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There are at least four primary sources of uncertainty or error that combine to set the practical upper limit of ^{14}C dating of terrestrial samples: (1) lack of sample integrity (i.e., complete *in situ* replacement of primary C via chemical or isotopic exchange), (2) incomplete removal of secondary (contaminant) C species during chemical pretreatment, (3) atmospheric C that is introduced to the original sample C during extraction, graphitization, and/or storage, and (4) uncertainties associated with AMS measurements. Analytical uncertainties associated with AMS measurements are largely unavoidable, but are usually stable and quite small. For example, the AMS measurement uncertainties for the samples measured in this study were typically only ~ 0.02 percent modern carbon (pMC; 2σ). Regarding (1), there is little that geochronologists can do to produce reliable ^{14}C ages from materials that have undergone complete chemical or isotopic exchange with environmental C species during burial. Once the original carbon inventory is lost, reliable ^{14}C ages cannot be recovered.

The primary challenges facing most geochronologists dating samples in the 40–60 ka time range, therefore, are removing contaminant C from the original sample C by chemical pretreatment, and physically isolating sample C from atmospheric C during extraction, graphitization, and storage. For most organic samples, the standard acid–base–acid (ABA) treatment that is used by all ^{14}C laboratories is sufficient to remove contaminant C species. However, the small amount of secondary C ($< 1\text{--}2\%$) that is left behind by the ABA treatment (e.g., Hatté et al., 2001) can result in significant errors for old samples because the impact of contamination increases with age

(Fig. 1). To address this issue, Bird et al. (1999) developed an aggressive chemical pretreatment technique which consists of the same initial acid and base steps that are used in the ABA treatment, followed by immersion of the base-insoluble fraction in an oxidizing solution ($0.1\text{ M K}_2\text{Cr}_2\text{O}_7$ in $2\text{ M H}_2\text{SO}_4$) for as long as the material can survive. This acid–base–wet oxidation technique, known as ABOX, removes more of the secondary C than the ABA method, but is limited to materials composed of elemental carbon, specifically charcoal and graphite.

In addition to developing the ABOX procedure, Bird et al. (1999) designed and constructed a vacuum extraction system at the Australian National University (ANU) that was dedicated to extracting carbon from old charcoal. Their system employed custom-designed, vacuum-backed valves and fittings, which were used to isolate sample C from atmospheric C during the extraction and graphitization processes. In conjunction with the ABOX pretreatment, they achieved background levels of 0.04 ± 0.02 pMC based on analyses of Ceylon graphite, equivalent to a ^{14}C “age” of 62.8 ± 5.6 ka for a 1 mg target. While highly effective, to our knowledge the ANU system has not been replicated in other ^{14}C laboratories. This may be due, in part, to higher costs and limited availability of the custom-designed valves and fittings, which also preclude retrofitting existing extraction lines. Another possible deterrent may be that a significant number of samples were lost during the graphitization process, likely because of sulfur poisoning or interference by other contaminant gases (M. Bird, pers. comm.). Regardless, we view the success of Bird and co-workers as a substantial leap forward in the quest to obtain reliable AMS ^{14}C ages for old samples.

At the University of Arizona’s Desert Laboratory, we recently constructed low-background extraction and graphitization systems that include technological and procedural improvements which increase the reliability of old ^{14}C ages, as well as the potential for adoption by other ^{14}C laboratories. The purpose of this paper is to describe these systems in detail and characterize their baseline conditions to help other laboratories pursue reliable AMS ^{14}C dating of old samples.

2. Methods

2.1. Low-background ^{14}C system—general

In contrast to Bird et al.’s systems, our low-background vacuum extraction system consists entirely of off-the-shelf or easily-fabricated parts (Fig. 2a). We use manual glass valves (4, 8, and 12 mm barrels with glass plugs; Kimble-Kontes) throughout the system with O-rings that are lightly greased with Apiezon[®] Type N (lower temperature) or T (higher temperature) vacuum grease. Based on system pressures, it appears that these greases take several days to degas and, therefore, following routine maintenance procedures, the system is allowed to pump down for at least a week to reach background pressure.

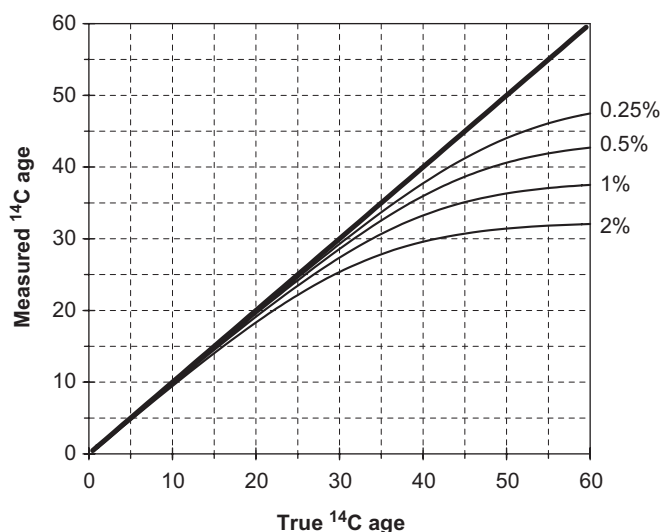


Fig. 1. Impact of modern contamination (0.25–2% by weight) on measured ^{14}C ages (thin lines) compared to the 1:1 or uncontaminated line (thickest line). Contamination can result from incomplete removal of secondary C species that are introduced during burial, atmospheric C species that are introduced during laboratory processing, or by sample crosstalk.

Sample and breakseal tubes are connected to the extraction system using Cajon Ultra-Torr[®] fittings with Viton[®] O-rings, which also take 2–3 days to fully degas when replaced. The system is evacuated by an oil-free turbomolecular pump (Varian TV-301 Navigator) backed by a dry scroll pump (Varian SH-100). All glass and metal surfaces, except those near cold traps and pressure gauges, are wrapped in flexible heat tape and held at $\sim 60\text{--}70^\circ\text{C}$ to minimize gas sorption on interior surfaces.

The graphitization system is physically separate from the extraction system (Fig. 2b). While the same type of glass valves (4 mm barrels with glass plugs; Kimble–Kontes) are used, the graphitization system is evacuated by a 63/150 mm BOC Edwards Diffstak[®] diffusion pump backed by a two-stage BOC Edwards Model E2M8 rotary pump. Oil vapors backstreaming from the diffusion pump are mitigated by an internal water-cooled baffle. Vapors from the rotary pump are prevented from backstreaming into

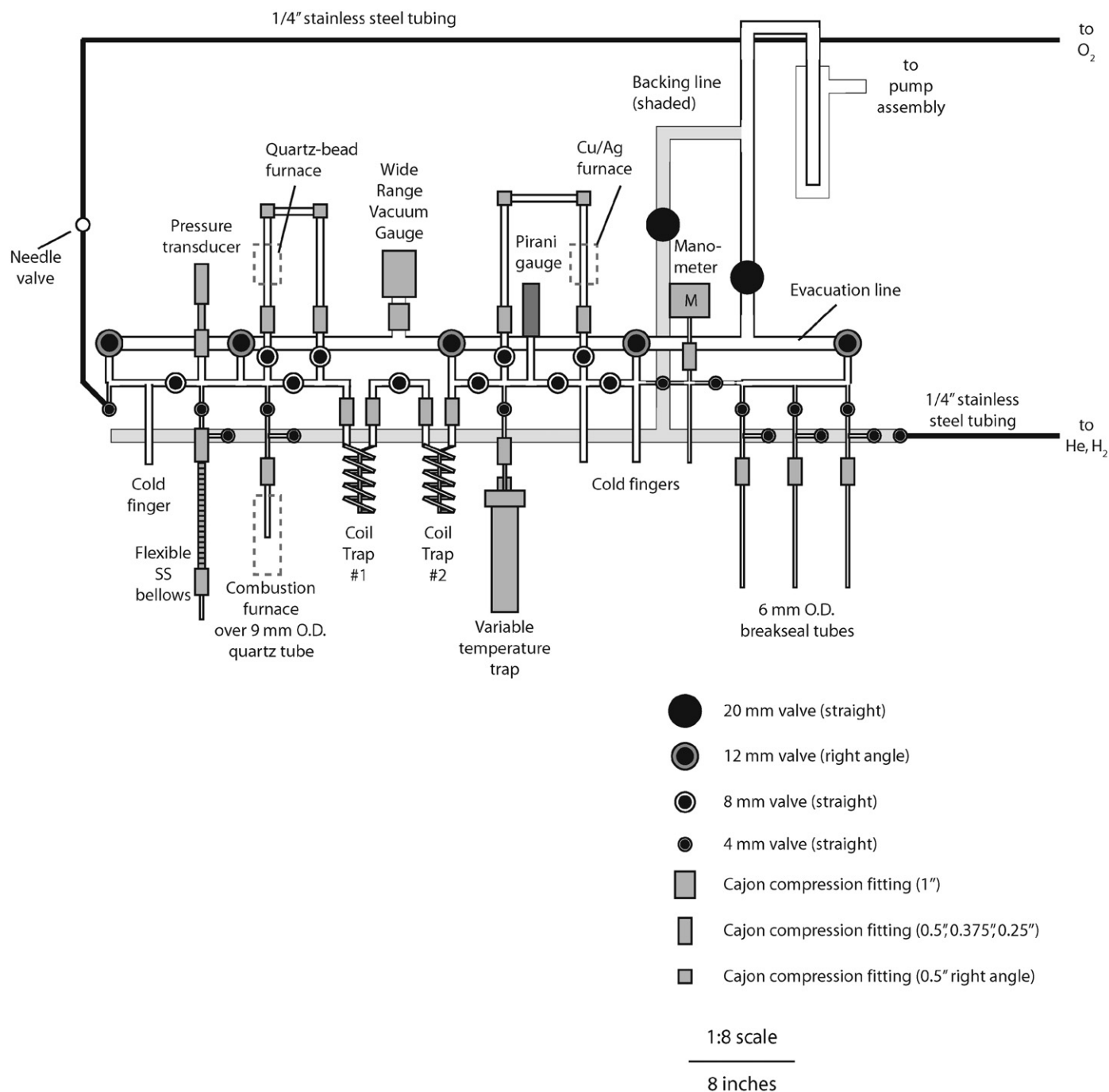


Fig. 2. Diagrams of (A) the low-background ^{14}C extraction system and (B) the graphitization system that we have constructed at the University of Arizona's Desert Laboratory. Legends and scales for both are shown in (A). Note that our graphitization system actually consists of 8 graphitization chambers but, for simplicity, only 4 are shown here.

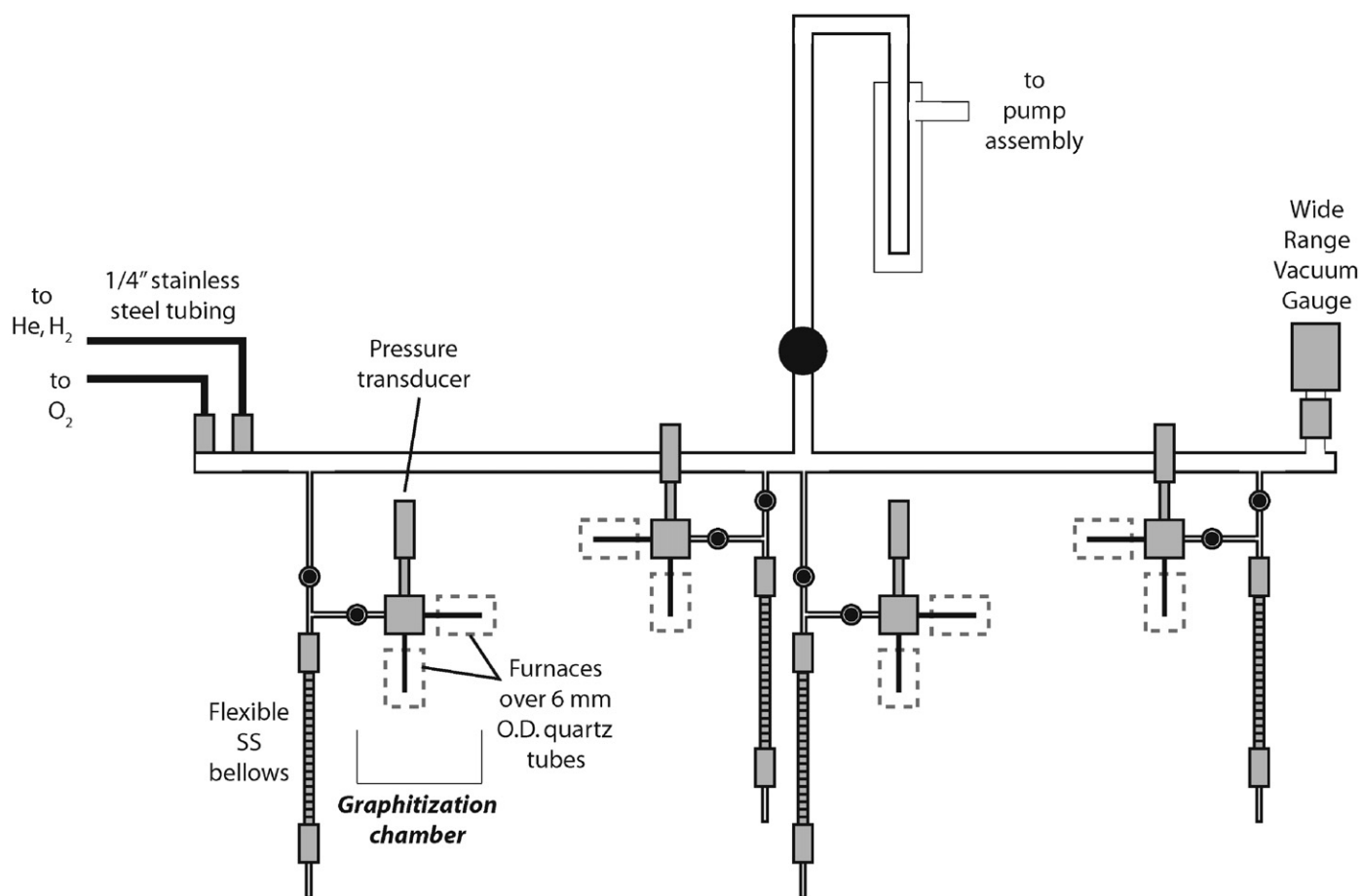


Fig. 2. (Continued)

the system by a molecular sieve foreline trap filled with 5 mm diameter activated alumina balls (replaced annually). Again, heat tape held at 60–70 °C is wrapped around all glass and metal surfaces except for the graphitization chambers.

Temperatures of furnaces used in both systems are held to within $\pm 5^\circ\text{C}$ of the desired temperature by a thermal control system (TCS). The TCS consists of a multi-channel console that contains individual temperature controllers for each furnace. Each controller constantly monitors the temperature of a thermocouple that is permanently cemented into a furnace chamber. Within each controller, the temperature sensing circuitry includes noise rejection filters and cold junction compensation. A servo feedback loop tuned to the thermal inertia of the furnace keeps the temperature at the set point by regulating the furnace power via pulse width modulation. The system is biased to minimize overshoot so that changes in conditions at the furnace, such as inserting a cold sample tube, result in rapid temperature recovery and fast dampening while avoiding high-temperature spikes.

The TCS allows us to avoid using variable autotransformers, commonly known as variacs, which are plugged into 115 V outlets and simply divide the outlet voltage. Using variacs, furnace temperatures remain dependent on the unregulated line voltage, which varies in our laboratory

by as much as 10%, as well as ambient temperature. The TCS enables the controller to maintain furnace temperatures to within 5°C of the set point over a range from 240 to 1020 °C, regardless of variations in the line voltage and ambient temperature.

2.2. Sample materials

We used several aliquots of Ceylon graphite to determine the total procedural blank for our extraction and graphitization systems, as well as the relationship between graphite mass and ^{14}C activity. Ceylon graphite is a naturally occurring, geological graphite that contains few, if any, primary ^{14}C atoms and is the same material that Bird et al. (1999) used to determine their background level. We also used 2 aliquots of a naturally-occurring charcoal (Rio Frio ash) to determine the proper stepped-combustion temperatures for charcoal as compared to graphite (see Section 3). We did not measure the ^{14}C activity of the Rio Frio ash for this study.

2.3. Pretreatment

All chemical pretreatment steps were carried out in capped vials or under a HEPA-filtered laminar flow hood.

All vials, pipette tips, glass jars, and a mortar and pestle used in the pretreatment process were cleaned in sub-boiling oxidation solution (0.1 M $\text{K}_2\text{Cr}_2\text{O}_7$ in 2 M H_2SO_4) for at least 2 h. These implements were then washed 3 times in 18.2 M Ω Milli-Q[®] water (hereafter Milli-Q) and stored in Tupperware for later use. Metal implements, including forceps and spatulas, were cleaned using a 1% Liquinox[®] solution in an ultrasonic bath for 1 h, rinsing 3 times in Milli-Q, sonicating for 1 h in Milli-Q, and then repeating the rinsing and sonication steps again. Pyrex[®] and quartz tubes used in the extraction and graphitization procedures were preheated to 600 and 900 °C, respectively, in the presence of research-grade ultra-high-purity (UHP) O_2 (99.999%) for at least 4–6 h.

Following Bird et al. (1999), sample fragments were handpicked and, if necessary, crushed to <1 mm diameter with a precleaned agate mortar and pestle. Approximately 15–25 mg of sample material were placed in a precleaned 50 ml Falcon[®] polypropylene centrifuge tube and subjected to the ABOX treatment as follows:

- 20 ml of 6 N HCl for 1 h to remove carbonate minerals;
- 30 ml of 1:1 HF/HCl overnight (if necessary) to remove silicate minerals;
- 50 ml of 1 M NaOH for 30 min to remove humic acids and other base-soluble organic compounds;
- 30 ml of 0.1 M $\text{K}_2\text{Cr}_2\text{O}_7$ in 2 M H_2SO_4 to remove non-elemental C compounds.

For the materials treated in this study (Ceylon graphite, charcoal), the duration of the oxidation step varied between 14 and 24 h. Yields decreased significantly beyond 24 h. All chemical reactions took place in a temperature-regulated hot box held at 60 ± 1 °C. Samples were rinsed 3 times in Milli-Q water between each step. The supernatant was removed after each rinse using an Eppendorf[®] 0–5 ml pipette and precleaned pipette tips or by centrifuging and decanting.

After the final rinse, the particulate material, referred to as oxidation-resistant elemental carbon (or OREC) by Bird et al. (1999), was suspended in Milli-Q and transferred under a HEPA-filtered laminar flood hood into a precleaned 5 ml glass vial using a Finnpiptette[®] 100–1000 μl micropipette and precleaned tips. Milli-Q was then added to and removed from the glass vial several times using the pipette to remove fine particulate matter and to further leach the oxidation solution from the OREC. The vial containing the cleaned OREC was covered with aluminum foil and dried in a vacuum oven at 70 °C overnight. Typical pretreatment yields for the Ceylon graphite and Rio Frio ash were 60–70% and 40–50%, respectively.

2.4. Combustion and extraction

The OREC was weighed and placed in a small (6 mm O.D., 4 mm I.D. \times 10 mm in length) precleaned quartz

tube, which itself was placed inverted into a larger (9 mm O.D., 7 mm I.D. \times 125 mm in length) precleaned quartz tube. The smaller quartz tube was handled with powder-free latex cleanroom gloves to prevent the introduction of finger grease into the extraction system. The inverted tube prevents particulates from being sucked out of the sample tube and into the extraction system during combustion. Whenever the line was opened to the atmosphere, either to load samples or breakseal tubes, it was backflushed with +2–4 psig (i.e., 2–4 psi above ambient air pressure) of research-grade UHP He (99.9999%) to minimize the entry of atmospheric gases into the extraction system. Prior to opening the breakseal or sample tube to the main vacuum system, He and atmospheric gases were removed via a separate backing manifold (Fig. 2a) to prevent contamination of the main line by atmospheric carbon. Pyrex[®] breakseal tubes (6 mm O.D.) were attached to the line with a Cajon[®] union (Fig. 2a), and heated under vacuum to approximately 500 °C using a glassblower's torch (avoiding the O-rings in the Cajon[®] fitting) until background pressures were reattained. A furnace set at 240 °C was then placed over the quartz combustion tube for 1 h to drive off water vapor and other sorbed atmospheric gases.

Approximately 0.5 atm of UHP O_2 was then introduced to the combustion chamber and quartz bead furnace area (Fig. 2a), and the temperature of the combustion furnace was raised to 500 °C for 30 min. The quartz bead furnace, which consists of a 12 mm O.D. diameter fused quartz tube packed with 2 mm diameter quartz beads, is maintained at ~ 1000 °C to promote the conversion of CO–CO₂ in the presence of O_2 (Lifton et al., 2001). Evolved sample gas and the O_2 carrier gas were then expanded into Coil Trap 1 (Fig. 2a), which was held at -190 °C with liquid nitrogen (LN) for 15 min to collect CO₂. Untrapped gases were then expanded into Coil Trap 2, which was also chilled with LN, for an additional 15 min. This step-wise procedure is designed to fully recover CO₂ that is produced during each combustion step.

Excess O_2 was then pumped slowly away through the coil traps, which were still immersed in LN, to capture any remaining CO₂ molecules. The trapped gases, including the sample CO₂, were then cryogenically transferred to the variable temperature trap (VTT), which consists of a 9 mm O.D. stainless-steel (SS) cold finger that is surrounded by a coiled cable heater and placed inside a 50 mm O.D. SS canister (modified after Lifton et al., 2001). The internal space of the VTT is filled with 10 psig of He to facilitate heat transfer between the cable heater and 9 mm SS tube. Type T thermocouples are silver-soldered to the top and bottom of the 9 mm tube to monitor temperatures inside the VTT. The sample was frozen into the cold finger by immersing the canister in LN for 15 min. By applying power to the cable heater with a variac while the canister remains immersed in LN, we can vary the temperature in the cold finger between 25 and -190 °C.

The internal temperature of the VTT was slowly raised to -120 °C and held constant for 15–45 min, depending on

the CO₂ yield, to remove water vapor and some condensable gases. CO₂ and other gases that sublimated from the VTT at this temperature flowed through a Cu/Ag trap held at 600 °C to remove SO_x, NO_x, and halide species. Sample CO₂ was collected in the cold finger beneath this trap using LN (Fig. 2a). Note that the Cu/Ag trap is reduced with 0.5 atm of H₂ periodically to remove oxides that build up on the Cu and Ag surfaces. After warming the cold finger to room temperature, an ethanol-LN slush bath held at –85 °C was placed on a second cold finger to remove any residual water vapor. The final CO₂ yield was measured in a known volume adjacent to the second cold finger using an MKS Baratron® 622A capacitance manometer. After the yield measurement, the CO₂ aliquot was cryogenically transferred to a Pyrex® breakseal tube and cut off with a glassblower's torch.

These procedures were repeated at each combustion temperature (500 and 850 °C). Between each temperature step, the VTT was baked out at 150 °C until background pressures were reattained to minimize sample crosstalk. In practice, aliquots of CO₂ can be extracted from a sample at 3 different temperatures in a 7-h period. At the end of each day, the entire system is filled with 0.5 atm of UHP He for 15 min and allowed to pump down overnight to remove any residual gases and to minimize sample crosstalk.

2.5. Graphitization

Breakseal tubes were scored with a glass-cutting knife and inserted into a 6 in flexible SS bellows (Fig. 2b). Iron powder (Alfa-Aesar, 6–10 µm APS, reduced, 99.5%) was loaded into a precleaned quartz tube (6 mm O.D., 75 mm in length) at a 2:1 ratio of Fe:C and attached vertically to the graphitization chamber using Ultra-Torr® compression fittings. Approximately 200 mg of Zn powder (Mallinckrodt, metal dust, 99.9%) was loaded into a second precleaned quartz tube (also 6 mm O.D., 75 mm in length) and attached horizontally to the graphitization chamber. Atmospheric gases were slowly pumped away to avoid disturbing the powders. Furnaces set at 325 °C were gradually moved onto the quartz tubes containing the Fe and Zn, and the system was allowed to pump down for 1 h after reaching background pressure to drive off water vapor and other sorbed atmospheric gases.

With the furnaces set at 325 °C still in place over the quartz tubes, approximately 0.5 atm of UHP O₂ was introduced to the graphitization system. The purpose of this step is to oxidize and subsequently remove any C species that may still be sorbed to the Fe and Zn powders or to the inside of the graphitization chamber. Each chamber was isolated and the powders remained in O₂ for 2 h. At the end of this period, O₂ was slowly pumped out of the graphitization chamber to avoid disturbing the powders, and the system was pumped down to background pressure (~15 min). Then 0.5 atm of UHP He was allowed into the entire system for 15 min to “scrub” any remaining O₂ molecules. We use the term “scrub” because the smaller

He molecules essentially displace unwanted gas molecules from the inside of the system. Based on pump down times, it appears that the He scrubbing effectively removes all (or nearly all) residual O₂ molecules. Pump down times were substantially longer (by 50% or more) when this step was skipped. This is likely because H₂ used in the following step combines with residual O₂ to create water, which takes additional time to pump away.

After the He was evacuated and the system reached background pressure (~15 min), 0.5 atm of research-grade UHP H₂ (99.9999%) was introduced to the system to reduce the Fe and Zn powders to their original oxidation states. Furnace temperatures were held at 325 °C during this step as well. As before, the graphitization chambers containing the powders and H₂ were isolated for 2 h, then slowly evacuated.

Finally, after the system reached background pressure (~15 min), the graphitization chambers were isolated, breakseal tubes were cracked within the flexible SS bellows, and the CO₂ samples were cryogenically transferred to the quartz tubes containing the Fe powder. Temperatures in the horizontal and vertical furnaces were then raised to 425 and 600 °C, respectively. Horizontal furnaces are placed over the tubes containing Zn powder for 1 h to convert CO₂ to CO (Slota et al., 1987). (Note that we have conducted subsequent tests that indicate 15 min is sufficient for this step.) Vertical furnaces were then raised over the tubes containing Fe powder to convert CO to graphite. The pressure in each graphitization chamber was continually monitored using a Setra Model GCT225 pressure transducer connected to a Setra Model 330 in-line display. Complete conversion to graphite is typically done overnight (approximately 16–18 h).

2.6. Storage

When graphitization was complete, the graphite powder was transferred from the vertical quartz tube to a 5 ml glass vial and covered with a silicone septum and an open-topped polypropylene screw cap. A 10 ml gas-tight syringe was used to penetrate the septum, remove air from the vial, and then fill it with research-grade UHP Ar (99.9997%). This process was repeated twice to completely replace atmospheric gases with Ar. Each 5 ml vial was then placed inside a 20 ml glass vial and covered with a penetrable silicone-lined cap. The same procedure was used to replace atmospheric gases with Ar in the space between the vials. This procedure essentially creates double-walled protection for the graphite target that eliminates the possibility of atmospheric C interacting with the graphite. Graphite targets were stored in Ar until just before they were pressed into target holders and loaded into the accelerator mass spectrometer for analysis. In sum, the targets were exposed to the atmosphere for no more than 1–2 h.

3. Results

Stepped-combustion experiments were conducted on ABOX-treated and untreated aliquots of Ceylon graphite

and Rio Frio ash to quantify differences in CO₂ yield profiles between the materials. Stepped combustion is used to physically separate multiple carbon species, each of which may potentially have different ¹⁴C activities (Cachier et al., 1989; Količ, 1995; McGeehin et al., 2001). For graphite and charcoal, sorbed atmospheric C species and more labile C species that survive the chemical pretreatment appear to evolve at lower temperatures, whereas primary sample C evolves at higher temperatures (Bird et al., 1999). Knowledge of the combustion profile of a given sample material allows preheating at the maximum temperature that the material can withstand without losing significant quantities of sample C.

CO₂ yields were measured following combustion at 100 °C intervals between 300 and 900 °C (Table 1, Fig. 3). The combustion profiles of ABOX-treated versus untreated aliquots for both graphite and charcoal were similar, although CO₂ yields for the ABOX-treated samples were skewed slightly toward lower temperatures. More significantly, there were large differences in the combustion profiles *between* materials. For graphite, CO₂ yields were significant only when temperatures reached > 500 °C and maximum yields were achieved at 700 °C. In contrast, combustion of charcoal was complete at temperatures

≤ 500 °C and maximum yields were achieved at 400 °C. These results demonstrate that stepped-combustion temperatures must be tailored to the individual sample material. For graphite, we suggest preheating samples to 500 °C in UHP O₂ for 1 h and collecting sample C at 850 °C for 1 h. For charcoal, we suggest preheating samples to 325 °C in UHP O₂ for 1 h and collecting sample C at 625 °C for 1 h. We also recommend combustion of charcoal for an additional hour at 850 °C to verify that combustion was complete.

We then processed a total of 20 targets from 7 aliquots of Ceylon graphite that were treated with ABOX and 4 targets from 2 aliquots that were not chemically treated to determine the total procedural blank level of our system. These experiments were also designed to quantify the relationship between the blank level of our system and the mass of the graphite target. Previous researchers have found an inverse relationship between blank levels and mass (Vogel et al., 1987; Donahue et al., 1990; Lifton et al., 2001), although their blank levels were higher than those measured in this study. The results (Table 2, Fig. 4) did not show a significant difference between the ABOX-treated and untreated populations, which suggests that there are few, if any, ¹⁴C atoms present in the Ceylon graphite itself.

Table 1
Summary of data for stepped-combustion experiments

Material	Pretreatment	Mass (mg)	Lab #	Temp (°C)	CO ₂ yield (μg)	% of total
Ceylon graphite	Untreated	5.69	LL-5a	300	4 ± 1	0.1 ± 0.0
			LL-5b	400	3 ± 1	0.1 ± 0.0
			LL-5c	500	10 ± 1	0.2 ± 0.0
			LL-5d	600	373 ± 5	6.9 ± 0.1
			LL-5e	700	2953 ± 43	54.6 ± 1.0
			LL-5f	800	2060 ± 30	38.1 ± 0.7
			LL-5g	900	9 ± 1	0.2 ± 0.0
					Total recovery	95.1 ± 0.9
Ceylon graphite	ABOX	3.57	LL-9a	400	4 ± 0	0.1 ± 0.0
			LL-9b	500	79 ± 1	2.2 ± 0.0
			LL-9c	600	1003 ± 13	27.8 ± 0.4
			LL-9d	700	1967 ± 25	54.4 ± 0.8
			LL-9e	800	560 ± 7	15.5 ± 0.2
			LL-9f	900	2 ± 0	0.1 ± 0.0
					Total recovery	101.2 ± 0.8
Rio Frio ash (charcoal)	Untreated	4.96	LL-6a	300	158 ± 2	6.3 ± 0.1
			LL-6b	400	1997 ± 29	79.4 ± 1.5
			LL-6c	500	349 ± 5	13.9 ± 0.3
			LL-6d	600	7 ± 1	0.3 ± 0.0
			LL-6e	700	3 ± 1	0.1 ± 0.0
			LL-6f	800	1 ± 1	0.1 ± 0.0
					Total recovery	50.7 ± 0.6
Rio Frio ash (charcoal)	ABOX	1.84	LL-21a	300	92 ± 1	10.2 ± 0.2
			LL-21b	400	813 ± 11	89.4 ± 1.6
			LL-21c	500	1 ± 0	0.2 ± 0.0
			LL-21d	600	1 ± 0	0.1 ± 0.0
			LL-21e	700	1 ± 0	0.1 ± 0.0
			LL-21f	800	1 ± 0	0.1 ± 0.0
					Total recovery	49.4 ± 0.6

All uncertainties are given at the 95% (2σ) confidence level.

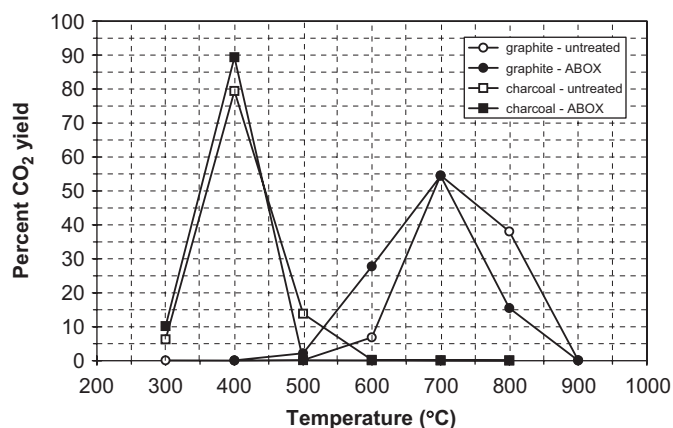


Fig. 3. CO₂ yield results from stepped-combustion experiments for Ceylon graphite and Rio Frio ash. Error bars reported at the 95% confidence interval ($\pm 2\sigma$) are smaller than the symbols shown. The difference in combustion profiles between the two materials demonstrates that stepped-combustion temperatures must be tailored to the individual sample type.

It also suggests that our procedures do not introduce significant quantities of modern C. The background level of our system is characterized by a non-linear, inverse relationship with sample mass between 92 and 1100 $\mu\text{g C}$ (adjusted $R^2 = 0.75$; $n = 24$). For a 0.5 mg target, the total procedural blank is 0.10 ± 0.02 pMC (2σ), equivalent to a ^{14}C “age” of 55.5 ± 1.8 ka. For a 1 mg graphite target, the total procedural blank is approximately 0.05 ± 0.01 pMC, equivalent to a ^{14}C “age” of 61.1 ± 1.8 ka.

Finally, to test the effectiveness of our storage procedures, we completed an additional set of experiments in which graphite targets of similar mass were stored in (1) air ($n = 2$), (2) UHP Ar ($n = 4$), and (3) UHP Ar as described above, but then exposed to air for 24 h after being pressed into targets ($n = 2$) (Fig. 5). The idea behind the latter split was that it would be more convenient for AMS personnel if they could press the graphite powder into targets the day before they were loaded into the accelerator, rather than immediately before loading. The results show that while there is a positive relationship between the measured ^{14}C activity and the duration that the graphite target was exposed to atmospheric C, it does not appear to be significant at the 95% confidence level (2σ).

Table 2
Summary of data for Ceylon graphite

Lab #	AMS #	Pretreatment	Mass (μg) ^a	pMC	^{14}C age (ka) ^b		
						+	–
LL-11a	67752	ABOX	556 ± 7	0.07 ± 0.02	58.0	2.5	1.9
LL-11b	67752	ABOX	737 ± 10	0.05 ± 0.02	60.7	3.7	2.5
LL-11c	67752	ABOX	868 ± 11	0.04 ± 0.02	62.5	5.0	3.1
LL-15a	67752	ABOX	427 ± 6	0.13 ± 0.02	53.5	1.3	1.1
LL-15b	67752	ABOX	317 ± 4	0.15 ± 0.02	52.4	1.1	1.0
LL-16a	67752	ABOX	727 ± 9	0.08 ± 0.02	57.4	2.3	1.8
LL-16b	67752	ABOX	538 ± 7	0.10 ± 0.02	55.6	1.8	1.5
LL-16c	67752	ABOX	403 ± 5	0.11 ± 0.02	54.9	1.6	1.3
LL-16d	67752	ABOX	223 ± 3	0.17 ± 0.04	51.4	2.1	1.7
LL-16e	67752	ABOX	166 ± 2	0.17 ± 0.02	51.4	1.0	0.9
LL-16f	67752	ABOX	92 ± 1	0.30 ± 0.16	46.5	5.8	3.3
LL-17a	67752	ABOX	379 ± 5	0.11 ± 0.02	54.9	1.6	1.3
LL-17b	67752	ABOX	210 ± 3	0.15 ± 0.02	52.4	1.1	1.0
LL-17c	67752	ABOX	456 ± 6	0.13 ± 0.02	53.5	1.3	1.1
LL-19a	67752	ABOX	502 ± 7	0.11 ± 0.02	54.9	1.6	1.3
LL-19b	67752	ABOX	661 ± 9	0.10 ± 0.02	55.6	1.8	1.5
LL-32a	67752	ABOX	900 ± 12	0.07 ± 0.02	58.5	2.7	2.0
LL-32b	67752	ABOX	843 ± 11	0.10 ± 0.02	55.6	1.8	1.5
LL-32c	67752	ABOX	1100 ± 14	0.04 ± 0.02	62.4	5.0	3.0
LL-33b	67752	ABOX	927 ± 12	0.07 ± 0.02	58.5	2.7	2.0
LL-12a	67752	Untreated	594 ± 8	0.09 ± 0.02	56.5	2.0	1.6
LL-14a	67752	Untreated	420 ± 5	0.11 ± 0.02	54.9	1.6	1.3
LL-14b	67752	Untreated	313 ± 4	0.11 ± 0.02	54.9	1.6	1.3
LL-14c	67752	Untreated	911 ± 12	0.08 ± 0.02	57.4	2.3	1.8

All uncertainties are given at the 95% (2σ) confidence level.

^aCO₂ yields for graphite combusted at 850 °C in UHP O₂. CO₂ yields at 500 °C were negligible.

^bCorrection for fractionation was done using a measured $\delta^{13}\text{C}$ value of $-6.8\text{‰}_{\text{vpdb}}$.

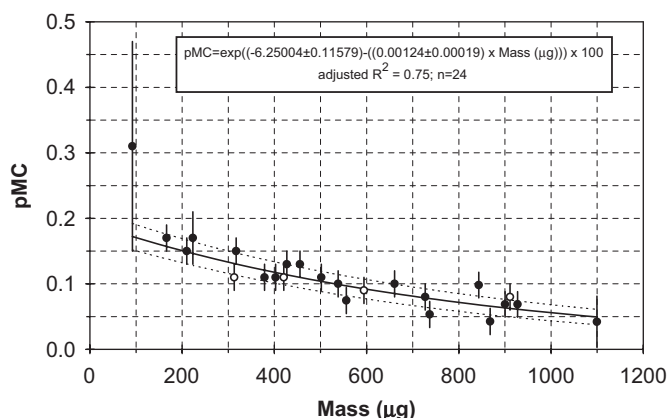


Fig. 4. Mass dependence of measured pMC of Ceylon graphite ($n = 24$), which represents the total procedural blank for our low-background ^{14}C system. Closed circles represent aliquots that were treated with ABOX ($n = 20$), open circles represent untreated aliquots ($n = 4$). Error bars for individual measurements and for the non-linear fit are given at the 95% confidence interval ($\pm 2\sigma$). Weighting of individual data points was done using the corresponding $1/\sigma^2$ values. For a 0.5 mg target, the total procedural blank is 0.10 ± 0.02 pMC (2σ), equivalent to a ^{14}C “age” of 55.5 ± 1.8 ka. For a 1 mg graphite target, the total procedural blank is approximately 0.05 ± 0.01 pMC, equivalent to a ^{14}C “age” of 61.1 ± 1.8 ka.

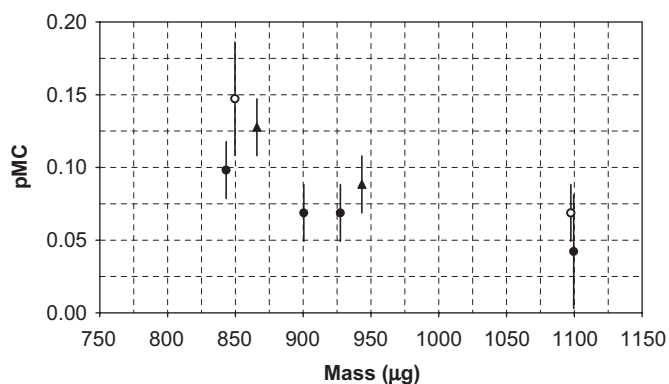


Fig. 5. Results of storage experiments using Ceylon graphite. Samples were treated by ABOX, split as CO_2 aliquots during extraction, graphitized, and then stored in UHP Ar (closed circles), air (open circles), or UHP Ar plus air for 24 h (closed triangles).

4. Discussion

4.1. Practical limits of our systems

The blank levels presented above should not be mistaken for the upper limit of ^{14}C ages that could potentially be obtained using the ABOX pretreatment and our extraction and graphitization systems. For any ^{14}C age to be considered reliable, the measured ^{14}C activity of the sample must be statistically distinguishable from the background level at the 95% confidence level (2σ). If it is not, then the sample age is considered to be “infinite”. For a 1 mg target, therefore, the practical limit of our system is ~ 55 ka; for a 0.5 mg target, the practical limit is ~ 50 ka.

These limits, of course, assume that the measured ^{14}C activity of Ceylon graphite actually represents the back-

ground level of our systems. Instead of Ceylon graphite, we could have used a naturally-occurring, ^{14}C -free charcoal to determine the practical limits of our system. After all, charcoal is abundant in the geological and archeological records, whereas geological graphite is not. The reason that we avoided using old charcoal to determine our background level is because it is possible, if not likely, that the measured ^{14}C activity of naturally-occurring old charcoal is a function of two processes: (1) the number of ^{14}C atoms that are introduced during laboratory processing of the sample; i.e., the true background level of the system, and (2) the number of ^{14}C atoms introduced during burial that are not removed by chemical pretreatment. For example, Bird et al. (1999) found that the ^{14}C activity of a reportedly “ ^{14}C -free” natural charcoal (Black Mountain charcoal) treated by ABOX was significantly higher than the ^{14}C activity of the Ceylon graphite. Yet, if the contaminant ^{14}C atoms were fully removed from the charcoal by the ABOX pretreatment, then the ^{14}C activity of the Black Mountain charcoal would have been identical to the ^{14}C activity of the Ceylon graphite. The implication of their results is that some number of ^{14}C atoms that were introduced to the charcoal during burial (i.e., contaminant C) survived the ABOX pretreatment. If true, then blank levels that are determined using this material would be too high.

Thus, it was our intention while building and characterizing our low background system to address only the true blank level of our system. While it is possible that the Ceylon graphite contains some inherent ^{14}C atoms, we did not find a difference between the untreated and ABOX-treated aliquots, which suggests that if inherited ^{14}C atoms were present, they were few in number and were not removed by the ABOX treatment. Moreover, the measured ^{14}C activities for the Ceylon graphite are consistent, predictable according to their mass, and as low as the Arizona-NSF AMS facility has ever measured (G. Burr, pers. comm.), which implies that the true limitation of a given background measurement for our system may actually be the AMS measurement limit itself. Thus, in our view, the background level, and hence the practical limit, of our extraction and graphitization systems is best represented by the measured ^{14}C activity of Ceylon graphite.

4.2. Elimination of graphitization problems

We have avoided problems with incomplete graphitization that were experienced by Bird et al. (M. Bird, pers. comm.) by (1) adopting rigorous cleanup procedures to remove contaminant gases from the sample C, and (2) keeping the oxidation and reduction temperatures relatively low. As described in Section 2.4, we use a variable temperature trap and a Cu/Ag trap held at 600°C to quantitatively remove SO_x , NO_x , and halide species from the sample CO_2 . These traps were first adopted by our research group at the University of Arizona when we experienced episodic problems with incomplete

graphitization while working with low levels of cosmogenically-produced ^{14}C (Lifton et al., 2001; Pigati, 2004). These problems have effectively been eliminated since the traps were put into place. At the onset of the present study, we encountered incomplete graphitization when we oxidized, scrubbed, and reduced the Fe and Zn powders at 600 and 425 °C, respectively. We eliminated this problem by reducing furnace temperatures to 325 °C during the redox and scrubbing procedures.

5. Conclusions

We recently constructed low-background vacuum extraction and graphitization systems that are dedicated to preparing old (40–60 ka) samples for ^{14}C dating. The challenges of ^{14}C dating in this time range are well known, chief among them is that the impact of contamination increases with sample age. Our systems and laboratory protocols were designed to minimize the possibility of introducing contaminant C, specifically atmospheric C, to the sample during extraction, graphitization, and/or storage. Our system employs only off-the-shelf or easily-fabricated parts, can be used for both organic and inorganic samples (although background levels still need to be characterized for inorganic materials), and avoids problems with incomplete graphitization. Thus, it can be used as a prototype for new extraction systems in other laboratories or as a guide to retrofitting existing extraction systems for researchers interested in ^{14}C dating in this time range.

We determined the background level of our system by measuring the ^{14}C activities of multiple aliquots of ABOX-treated and untreated Ceylon graphite. The upper limit of ^{14}C dating for our systems depends on the mass of the graphite target. For a 1 mg target, the practical limit of our system is ~55 ka; for a 0.5 mg target, the practical limit is ~50 ka.

Finally, geochronologists widely recognize that the reliability of ^{14}C dating quickly degrades as the measured ^{14}C age exceeds 40 ka. For example, Bird and co-workers have clearly demonstrated that ^{14}C ages of old samples that are obtained using standard chemical and extraction techniques often underestimate true ^{14}C ages by 8–10 ka or more (Bird et al., 1999; Turney et al., 2001a, b, c; Bird et al., 2003; Santos et al., 2003). Thus, we urge researchers (geologists and archeologists alike) to exercise extreme caution when interpreting published ^{14}C ages in excess of 40 ka BP. While we are not suggesting that all reported ^{14}C ages in excess of 40 ka are erroneous, without such caution, interpretations of the timing of geological or archeological events may, in fact, be based on measured levels of contamination, rather than sound chronologic data.

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